(vinegar essence) to 63,762 μg/100 g (cloves). Spices (av. 5555 μg/100 g) had the widest range of Mn contents and dairy products (av. 26 μg/100 g) the narrowest range.

— — — —

109: 148250w **Modern Nutrition Science, 14: Food Santitation and Microbiology.** (Gendaijin no Eiyogaku, 14: Shokuhin Eiseigaku, Biseibutsugaku) Morishita, Yoshiyuki; Ohmori, Toshio; Editors (Asakura Publishing Co., Ltd.: Tokyo, Japan). 1987. 221 pp. (Japan) ¥2200.

109: 148251x **Membrane Filter and Food Microbiology.** Sharpe, A. N.; Peterkin, P. I. (Wiley: New York, N. Y.). -1987. 323 pp. (Eng) $83.95.

109: 148252y **Modern Nutrition Science, 5: Public Health.** (Gendaijin no Eiyogaku, 5: Koshu Eiseigaku) Kashiwazaki, Hiroshi; Editor (Asakura Publishing Co., Ltd.: Tokyo, Japan). 1987. 202 pp. (Japan) ¥2200.

— — — —

109: 148253z **Antimicrobial medium for low-temperature sterilization of glass containers for foods.** Preusse, Rolf; Reiniger, Werner; Neubert, Siegfried; Schmidt, Klaus Dieter; Cersovsky, Herbert; Hambrock, Dieter; Mann, Gertraud (VEB Chemiekombinat Bitterfeld) Ger. (East) DD 243,813 (Cl. A61L2/16), 18 Mar 1987, Appl. 262,486, 30 Apr 1984; 3 pp. An antimicrobial medium for low-temp. sterilization, e.g. in washing machines, of glass containers for foods contains 2–10% Na or K peroxydisulfate. The above medium is claimed. The medium is aq. and contains 0.5–1.0% active ingredient for use at 48–55°. High quality hygiene is guaranteed with the claimed medium. Complete packaging under such conditions allows long term storage stability. An aq. soln. contg. 1.0 and 0.7% of a cleaning mixt. (alkali metal hydroxide 40, polymeric phosphate 35, water-free alkali silicate 15, K peroxydisulfate 5, surfactant 1, defoamer 0.025%, and filler q.s.) in the mild bath and spray sections of a washing machine, resp., these 2 sections being operated at 53 and 48°, resp., led to 87.0% germ-free glassware (<0.1/cm³) after washing for 7 min; controls showed 72.9% germ-free glassware after 85 and 80° (bath and spray, resp.) washing for 7 min.

109: 148254a **Process for the aromatisation of foodstuffs by yeast treatment, and foodstuffs obtained thereby.** Vladescu, Barbu Dinu Vladimir (Pernod, Ricard) Eur. Pat. Appl. EP 277,062 (Cl. A23L1/30), 03 Aug 1988, FR Appl. 87/501, 19 Jan 1987; 6 pp. Fruits or vegetable products, juices, fruit concs., and residues from the distn. of fruit juices are fermented with yeast or yeast ext. which have low esterase activities in order to regenerate or add a desired aroma. Thus, pear conc. 200 mL was cultured with 10^8 *Pachysolen taumophilus* for 16 h at 25° with shaking. The esterase activity of the yeast was 1.8 μmol *p*-nitrophenol released/10 min/mg protein. The original aroma was regenerated.

109: 148255b **Preservation of solid feed with sorbates and acids or acid salts.** Remmert, Karl Heinz; Lueck, Erich (Hoechst A.-G.) Ger. Offen. DE 3,701,567 (Cl. A23K3/00), 04 Aug 1988, Appl. 21 Jan 1987; 4 pp. A method for preservation of feed with sorbates 2×10^{-4} to 2×10^{-3} mol/100 g feed and with acids or acid salts (e.g. amidosulfuric acid, HSO_4 salts) 1–3 wt.%. At least 30% of the sorbate has a particle size < 300 μm. Thus, piglet feed mixed with sorbic acid 0.05% was preserved 17 days; that mixed with amidosulfuric acid 2.0% for 9 days, but that mixed with bath sorbic acid and amidosulfuric acid (at the same concns.) for > 1 mo.

109: 148256c **Ethanol-based food preservatives.** Suneya, Yoichi (Dover Japan, Inc.) Jpn. Kokai Tokkyo Koho JP 63,133,972 [88,133,972] (Cl. A23L3/34), 06 Jun 1988, Appl. 86/279,621, 26 Nov 1986; 4 pp. Food preservatives, useful for bakery products, fruits, and vegetables, contain 75–85 vol./vol.% EtOH, 1–3 wt./vol.% Na lactate (I), 0.5–1.5 wt./vol.% glycerin fatty acid esters, 0.02–0.05 wt./vol.% sucrose fatty acid esters, and 11–27 vol./vol.% H_2O. Thus, sponge cakes sprayed with a compn. of EtOH 77, I 2, glycerin fatty acid esters (mainly caprylic acid monoglyceride) 0.7, sucrose fatty acid esters 0.04, and H_2O 24.4% and stored in a container at 15° remained mold-free for 10 days while unsprayed cakes started to show mold growth on the 5th day.

109: 148257d **Preparation of calcium-rich permeate from dairy fluid for diet food or drink manufacture.** Van den Boogaard, Cornelis (Verenigde Cooperatieve Melkindustrie Coberco B. A.) Eur. Pat. Appl. EP 273,485 (Cl. A23C9/142), 06 Jul 1988, NL Appl. 86/2,991, 25 Nov 1986; 5 pp. A Ca-rich permeate useful for the manuf. of Ca-rich beverage or food is prepd. by subjecting milk, curd, casein, or other dairy fluid in acid condition to ultrafiltration. Skim milk was acidified to pH 4.5 by fermn. with lactic acid bacteria. The whey was sepd., pasteurized at 92° for 15 s, and subjected to ultrafiltration at 50°. The resulting filtrate contained 120 mg Ca/100g filtrate. The Ca to protein ratio was 407 mg/g.

109: 148258e **Powdered, water-soluble carotenoid preparations and a method for their manufacture.** Horn, Dieter; Lueddecke, Erik; Schaefer, Peter (BASF A.-G.) Ger. Offen. DE 3,702,030 (Cl. A23L1/275), 04 Aug 1988, Appl. 24 Jan 1987; 8 pp. The powd., water-sol. carotenoid compn. is prepd. by rapid dissoln. of a carotenoid, 1.5–20 wt.% (based on the carotenoid) edible oil, and an emulsifier in a water-miscible org. solvent. at 50–240°. The resulting soln. is mixed with an aq. soln. of a protective colloid at 0–50° to form a two-phase system contg. microdisperse carotenoid–oil droplets. The org. solvent and the water are then removed by std. methods to form the powder. Thus, β-carotene 5 g was suspended in 240 g soln. contg. ascorbylpalmitate 4, α-tocopherol 5, and peanut oil 20 g in isopropanol and rapidly mixed with 360 isopropanol at 225°. The resulting soln. was mixed with <1000 g soln. contg. gelatin 60 and saccharose 90 g. The resulting microdisperse oil droplets had an av. diam. 210 nm. The isopropanol was removed and the resulting viscous liq. was spray-dried. The powd. was redissolved in water to provide a microdisperse phase with particle size 220 nm.

109: 148259f **Manufacture of cheese aroma by fermentation of milk products with microorganisms.** Wink, Joachim; Fricke, Ulrich; Deger, Hans Mathias; Mixich, Johann; Bauer, Dieter; Justinski, Uwe (Hoechst A.-G.) Ger. Offen. DE 3,701,836 (Cl. A23L1/23), 04 Aug 1988, Appl. 23 Jan 1987; 3 pp. Thin layers of milk products, e.g. quark, yogurt, are fermented with microorganisms such as yeast (*Torulopsis*, *Candida*) or fungi (*Penicillium*) for 5–7 days and a cheese aroma is prepd. by extn. of the culture with an appropriate org. solvent.

109: 148260z **Coloring of foodstuffs with naturally occurring coloring materials.** Krauskopf, Heinz (Markt- und Kuehlhallen A.-G.) Ger. Offen. DE 3,701,993 (Cl. A23L1/275), 04 Aug 1988, Appl. 23 Jan 1987; 4 pp. Foodstuffs, e.g, fruits such as cherries and strawberries, are colored with naturally occurring coloring materials such as elderberry juice which are first concd. to ≥70 wt.% solid material. The concd. coloring material is added to the fruits in an aq. sugar soln. until the concn. of coloring material is 0.1–2.5 wt.% (based on the sugar soln.).

109: 148261a **concentration of vinegar by neutralization and distillation under acidic conditon.** Oonishi, Takashi (Sanei Chemicals Co., Ltd.) Jpn. Kokai Tokkyo Koho JP 63,137,669 [88,137,669] (Cl. C12J1/04), 09 Jun 1988, Appl. 86/285,227, 28 Nov 1986; 3 pp. Vinegar is concd. by neutralization with alkali, concn., and distn. in vacuo in the presence of excess acids. The method is far more efficient than the conventional freezing method. Vinegar (AcOH content 7.4%) was neutralized with NaOH, concd. at 60° and 40 mmHg (AcONa content 60%), and distd. in the presence of excess H_2SO_4 at 43° in vacuo to give concd. vinegar with 70.8% AcOH content.

109: 148262b **Proline and cystine for enhancing the flavor of Chinese noodles.** Okumura, Joji; Hayakawa, Toshihiko; Suzuki, Yasuko (Hasegawa, T., Co., Ltd.) Jpn. Kokai Tokkyo Koho JP 63,137,655 [88,137,655] (Cl. A23L1/16), 09 Jun 1988, Appl. 86/284,364, 01 Dec 1986; 4 pp. Flavorings for instant Chinese noodles are prepd. by heating a mixt. of proline (I) and cystine (II) in an aq. medium at pH ≥8. Thus, 2 g *L*-I and 3 g *L*-II were dispersed in 100 g 80% aq. glycerin, controlled at pH 11.5 with 30% aq. NaOH, mixed with 5 g wheat gluten, and heated at 105° for 3 h with stirring to give a product which showed a flavor characteristic of the freshly boiled raw Chinese noodles.

109: 148263c **Method of removing the bitter taste from potassium chloride by thaumatins.** Nakagawa, Takahiro (Sanei Chemicals Co., Ltd.) Jpn. Kokai Tokkyo Koho JP 63,137,657 [88,137,657] (Cl. A23L1/237), 09 Jun 1988, Appl. 86/285,225, 28 Nov 1986; 2 pp. The bitter taste of KCl is removed by addn. of ≤1% thaumatins. Thus, addn. of 0.6×10^{-3}% thaumatins to 0.5% aq. KCl reduced the bitter taste by ~75% as tested by a panel of 4 males and 6 females.

109: 148264d **Method of enhancing the saltiness of sodium chloride by thaumatins.** Nakagawa, Takahiro (Sanei Chemicals Co., Ltd.) Jpn. Kokai Tokkyo Koho JP 63,137,658 [88,137,658] (Cl. A23L1/237), 09 Jun 1988, Appl. 86/285,226, 28 Nov 1986; 2 pp. The saltiness of NaCl is enhanced by addn. of thaumatins to NaCl or its aq. soln. Thus, the saltiness of 0.8% aq. NaCl was enhanced by ~20% upon addn. of 0.2×10^{-3}% thaumatins as tested by a panel of 5 males and 5 females.

109: 148265e **Extracts from fermentation residue and their use as improvers for yeast-raised goods.** Tomlinson, John David; Robertson, Jennifer Anne; Thomson, William Kenneth (Weston, George, Foods Ltd.) PCT Int. Appl. WO 88 03,365 (Cl. A21D2/14), 19 May 1988, AU Appl. 86/8,813, 05 Nov 1986; 32 pp. Natural improvers for yeast-raised baked goods are extd. from fermn. residues. A concd. ext. was prepd. from semisolid brewery yeast residues by (*1*) dilg. the waste yeast with water; (*2*) autoclaving at 120° for 10 min to disrupt the cells and inactivate the enzymes; (*3*) cooling the mixt. to 4° and adjusting the pH to 4; and (*4*) removing the cell debris by centrifugation. The clear liquor (contg. NAD) was freeze-dried, ground, and mixed with an equal mass of wheat starch. Addn. of the resultant product to doughs contg. chem. improvers provided a significant increase in the loaf vol. It also provided a retardation in the staling or firming characteristics of the loaves.

109: 148266f **Process for preparing high protein bread with ascorbic acid and product.** Ferrara, Peter J. U.S. US 4,759,934 (Cl. 426–21; A21D2/22), 26 Jul 1988, US Appl. 778,887, 23 Sep 1985; 5 pp. Cont.-in-part of U.S. Ser. No. 778,887, abandoned. A process for producing yeast-leavened wheat bread with ≤45% protein (on a dry basis) comprises forming a dough contg. half baking flour, vital wheat gluten, steam-treated full fat wheat germ having substantially no glutathione and soy conc. (optionally steamed to eliminate sulfhydryl) sufficient to provide a final baked bread contg. ~18–25% protein (on a wet basis); 450–850 ppm ascorbic acid; K bromate 5–10% (based on ascorbate); and water. The dough is then fermented and baked.

109: 148267g **Malic acid and/or tartaric acid for pet foods for taste improvement.** Matsushita, Takejiro (Ajinomoto General Foods, Inc.) Jpn. Kokai Tokkyo Koho JP 63 24,860 [88 24,860] (Cl. A23K1/18), 02 Feb 1988, Appl. 86/168,701, 17 Jul 1986; 6 pp. Tartaric acid and/or malic acid are added to dry- or moist-type pet food to improve its taste. Thus, corn 26, flour 21, soybean cake 15, meat powder 17, fish powder 5, wheat germ 3, beer yeast 3, and vitamins and minerals 2 parts by wt. were kneaded, extruded, cut, dried, coated with 8 parts by wt. beef tallow, and sprinkled with

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 937 412 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.08.1999 Bulletin 1999/34

(51) Int Cl.[6]: **A23L 1/275**

(21) Application number: **99103239.2**

(22) Date of filing: **19.02.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **23.02.1998 EP 98103113**

(71) Applicant: **F. HOFFMANN-LA ROCHE AG**
4070 Basel (CH)

(72) Inventors:
- **Stein, Hermann**
  4410 Liestal (CH)
- **Viardot, Klaus**
  4125 Riehen (CH)
- **Yang, Bin**
  4313 Möhlin (CH)

(74) Representative: **Kellenberger, Marcus Dr. et al**
F.Hoffmann-La Roche AG
Grenzacherstrasse 124
4070 Basel (CH)

(54) Preparation of a finely divided pulverous carotenoid preparation

(57) The present invention relates to a continous process for the preparation of a pulverous carotenoid, retinoid or natural colourant preparation, wherein the active ingredient is finely divided, which process comprises the steps of

a) forming a suspension of the active ingredient in a water-immiscible organic solvent optionally containing an antioxidant and/or an oil,

b) feeding the suspension of step a) to a heat exchanger and heating said suspension to 100-250°C, whereby the residence time in the heat exchanger is less than 5 see,

c) rapidly mixing the solution of step b) at a temperature in the range of 20-100°C with an aqueous solution of a swellable colloid optionally containing a stabilizer,

d) removing the organic solvent and

e) converting the dispersion of step d) into a pulverous preparation.

EP 0 937 412 A1

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a continous process for converting carotenoids, retinoids or natural colourants into finely divided pulverous forms which are particular required for colouring foodstuff and animal feeds.

[0002] Various processes have been described to prepare a powder containing the active ingredients with a crystallite size less than 1 micron. Most of the processes are well suited to batch processing applications.

[0003] For example, US Patent 3,998,753 describes a batch process for the preparation of a water dispersible carotenoid containing powder, wherein the carotenoid has a particle size of less than 1 micron, which process comprises (a) forming a solution of a carotenoid and an antioxidant in a volatile solvent, said solvent being selected from the group consisting of halogenated aliphatic hydrocarbons such as chloroform, carbon tetra-chloride and methylene chloride; (b) forming an aqueous solution of sodium lauryl sulfate, a water soluble carrier composition such as e.g. gelatin, a preservative and a stabilizer, and adjusting said solution to a pH of about 10 to 11 and (c) forming an emulsion of the solutions of steps (a) and (b) by mixing at a high speed and high shear; removing the organic solvent and spray drying the resulting emulsion to obtain a carotenoid powder.

[0004] In the European Patent Publication EP-0065193 B1 or the corresponding US Patent 4,522,743 a continous process for the preparation of finely divided carotenoid powders is described, in which the carotenoid has a particle size essentially below 0.5 microns. The carotenoid is dissolved in a volatile, water miscible organic solvent within less than 10 sec. at 50-200°C. The carotenoid is immediately precipitated in colloidally dispersed form from the resulting molecularly dispersed solution by rapid mixing with an aqueous solution of a swellable colloid at 0-50°C. The preparation of the carotenoid solution and the precipitation of the carotenoid are effected continuously in two mixing chambers. The resulting dispersion is freed of solvent and the dispersing medium in a conventional manner.

[0005] However, for economical and ecological reasons this process has the disadvantage that a large amount of solvent must be used.

[0006] It is an object of the present invention to provide a process that overcomes the aforesaid drawback while converting the active ingredient into finely divided pulverous form.

[0007] It has now been found that it is possible to provide a pulverous preparation wherein the active ingredient is finely divided by using a water-inmiscible organic solvent in a continous process.

[0008] Thus, the present invention relates to a continous process for the preparation of a pulverous carotenoid, retinoid or natural colourant preparation, wherein the active ingredient is finely divided, which process comprises the steps of

a) forming a suspension of the active ingredient in a water-inmiscible organic solvent optionally containing an antioxidant and/or an oil,

b) feeding the suspension of step a) to a heat exchanger and heating said suspension to 100-250°C, whereby the residence time in the heat exchanger is less than 5 sec,

c) rapidly mixing the solution of step b) at a temperature in the range of 20-100°C with an aqueous solution of a swellable colloid optionally containing a stabilizer,

d) removing the organic solvent and

e) converting the dispersion of step d) into a pulverous preparation.

[0009] The term "finely divided" denotes in the scope of the present invention a particle size of less than 1.5 micron, preferably less than 1 micron, more preferably less than 0.4 micron.

[0010] The term "active ingredient" denotes in the scope of the present invention carotenoids, retinoids or natural colourants.

[0011] Carotenoids for the purpose of the present invention in particular include beta-carotene, beta-apo-4'-carotenal, beta-apo-8'-carotenal, beta-apo-12'-carotenal, beta-apo-8'-carotenic acid, astaxanthin, canthaxanthin, zeaxanthin cryptoxanthin, citranaxanthin, lutein, lycopene, torularodin-aldehyde, torularodin-ethylester, neurosporaxanthin-ethylester, zeta-carotene or dehydroplectaniaxanthin. Also included are carotenoids of natural sources. Preferred are beta-carotene, astaxanthin, canthaxanthin, beta-apo-8'-carotenal and lycopene; more preferred is beta-carotene.

[0012] Natural colourants for the purpose of the present invention in particular include curcumine, cochineal, carmine, annatto and mixtures thereof.

[0013] Preferably the process of the invention is carried out using carotenoids.

[0014] The temperature of step b) is preferably 120-180°C, more preferably 140-170°C and the temperature of step c) is preferably 50-80°C.

[0015] The residence time in the heat exchanger is preferably 0.5-4 sec, more preferably 1-3 sec.

[0016] The term "water-inmiscible organic solvent" denotes in the scope of the present invention an organic solvent having a solubility in water of less than 10% under atmospheric pressure. Suitable water-inmiscible organic solvents for carrying out the continous process according to the invention are halogenated aliphatic hydrocarbons such as e.g. chloroform, carbon tetra-chloride and methylene chloride, water-inmiscible esters such as e.g. carbonic acid dimethylester (dimethyl carbonate), formic acid ethylester (ethyl formate) methyl -, ethyl-, or isopropylacetate; or water-inmiscible ethers such as e.g. methyl-tert. butylether and the like. Preferred are dimethyl carbonat, ethyl formate, ethyl-, or

isopropylacetate, methyl-tert. butylether.

[0017] The term "swellable colloids" denotes in the scope of the present invention gelatin, carbohydrates such as e.g. starch or starch derivatives, dextrin, pectin, gum arabic, octenylbutanedioate amylodextrin (CAPSUL™), milk protein such as e.g. casein and vegetable protein as well as mixtures thereof. Preferred are fish gelatin or starch derivatives.

[0018] To increase the stability of the carotenoid it is advantageous to add an antioxidant being selected from the group consisting of ascorbic acid, ascorbylpalmitate, dl-alpha tocopherol, mixed tocopherols, lecithine, butylhydroxytoluol, butyl-4-methoxyphenol and combinations of these compounds.

[0019] The antioxidant can be added either to the matrix solution or to the carotenoid solution or to both solutions. A preferred antioxidant for the carotenoid solution is dl-alpha tocopherol and for the aqueous phase solution it is ascorbyl palmitate.

[0020] It may be further advantageous to dissolve an oil in the carotenoid suspension, preferrably corn oil.

[0021] Reference is now made to the accompanying drawing Fig. 1 where a flow chart suitable for carrying out the process in accordance with the instant invention is diagrammatically illustrated. The whole process has to be carried out continously.

[0022] The flow chart is explained as follows:

[0023] An aqueous matrix containing a swellable colloid and optionally a stabilizer is prepared in Kettle 1.

[0024] A suspension of a carotenoid in the selected solvent is prepared in Kettle 2. The suspension may further contain an antioxidant and an oil.

[0025] The carotenoid suspension is fed by pump 6 to the heat exchanger 4. The flow rate is adjusted according to the desired residence time which is necessary to dissolve the carotenoid in the solvent at a given temperature. In the heat exchanger 4 the carotenoid suspension is heated to 100 to 250 °C, preferably to 120 to 180 °C, more preferably to 140 to 170°C and the carotene is solubilized. The heating can be done either indirectly through the heat exchanger or directly by mixing with steam at 8. The residence time in the heat exchanger is less than 5 sec, preferably 1 to 3 sec.

[0026] The matrix solution of Kettle 1 is fed by pump 7 to Kettle 3. The flow rate depends on the suspension flow rate and the required emulsion composition. In Kettle 3 the carotenoid suspension and the matrix are mixed and emulsified by using a rotor stator homogenizer to the desired particle size of the inner phase of approx. 150-400 nm. As a result of the mixing the temperature is lowered to the range 20 to 100 °C.

[0027] The dispersion obtained passes to a second heat exchanger 5 whereby the dispersion is cooled. The pressure is released to atmospheric pressure by pressure control.

[0028] The solvent is removed using conventional methods e.g. by evaporation. A pulverous composition can be isolated from the resulting dispersion by conventional methods, for example by spray drying or by using powder catch technique.

[0029] Using this invention it is possible to manufacture powders which cover very wide range of color.

[0030] The manner in which the process of the invention may readily be carried out is illustrated by the following examples. The color intensity was measured in an aqueous dispersion containing 5 ppm carotenoid and given by the calculated extinction of 1% solution in a 1 cm cuvette (E1/1-value). The average particle size has been measured by Coulter Particle Analyzer N4S. The carotenoid content was measured by UV-spectroscopy.

Example 1

[0031] Solvent: ethyl acetate, indirect heat transfer.

[0032] The aqueous matrix was prepared in Kettle 1. Thus, 1.0 kg of ascorbyl palmitate was dispersed in 27.8 kg of water at 60°C. The pH-value of this dispersion was adjusted with NaOH (20%) to 7.2-7.6. Then 3.4 kg of fish gelatin and 7.2 kg of sucrose were added. The resulting mixture was stirred until a viscous, clear solution was obtained.

[0033] 0.75 kg of all-trans-β-carotene cryst. were dispersed in Kettle 2 in a mixture of 90 g of dl-α-tocopherol, 330 g of corn oil and 7.5 kg of ethyl acetate.

[0034] The carotene suspension was fed continuously at a rate of 6 kg/h via pump 6 to the heat exchanger 4, heated to 160°C and the carotene was solubilized. The residence time in the heat exchanger was 4 sec.

[0035] The matrix solution of Kettle 1 was fed via pump 7 with a flow rate of 9.2 kg/h to Kettle 3 and mixed with the carotene solution.

[0036] The resulting emulsion was cooled in a second heat exchanger 5 to 60°C and the pressure was released to atmospheric pressure.

[0037] Ethyl acetate was removed in a thin film evaporator. The resulting emulsion showed a particle size of the inner phase of 225 nm and was spray dried. A powder with the following specifications was obtained: 11.6 % carotene content, $E^{1}/_{1}$ = 1015, λ max. 440-460 nm. The powder was well soluble in cold water with an intense red coloration.

Example 2

Solvent: isopropyl acetate, direct heat transfer (steam)

[0038] 1.25 kg of Ascorbyl palmitate was dispersed in 30.9 kg water at 60°C according to Example 1. The pH-value of this dispersion was adjusted with NaOH (20%) to 7.2-7.6. Then 5.1 kg of fish gelatin and 7.1 kg of sucrose were added. The resulting mixture was stirred until a viscous, clear solution was obtained.

[0039] 0.75 kg of Canthaxanthin cryst. were dispersed in Kettle 2 in a mixture of 0.10 kg of dl-α-tocopherol, 0.36 kg of corn oil and 6.25 kg of isopropyl acetate.

[0040] The canthaxanthin suspension was fed continuously at a rate of 6 kg/h via pump 6 to the mixing chamber where the temperature was raised by injection of steam to 170°C. Then, the hot canthaxanthin dispersion passed within 2 sec. through the heat exchanger 4 where the canthaxanthin was solubilized.

[0041] The matrix solution of Kettle 1 was fed via pump 7 with a flow rate of 8.1 kg/h to Kettle 3 and mixed with the canthaxanthin solution.

[0042] The resulting emulsion is cooled in heat exchanger 5 to 60°C and the pressure was released to atmospheric pressure.

[0043] Isopropyl acetate was removed in a thin film evaporator. The resulting emulsion showed a particle size of the inner phase of 213 nm and was spray dried. A powder with the following specifications was obtained: 12.3 % canthaxanthin content, $E\,^{1}/_{1}$ =905, λ max. 470-485 nm. The powder was well soluble in cold water with an intense cherry-red coloration.

Example 3

Solvent: isopropyl acetate, direct heat transfer (steam)

[0044] 10.3 kg of Fish gelatin, 20.6 kg of sugar and 2.78 kg of ascorbyl palmitate were dissolved in 27.56 kg of water in Kettle 1. The pH-value of this matrix was adjusted with NaOH (20%) to 7.2 - 7.6.

[0045] 6.68 kg of β-Carotene, 0.84 kg of dl-α-tocopherol and 3.34 kg of corn oil were dispersed in 33.4 kg of isopropyl acetate in Kettle 2.

[0046] The β-carotene suspension was fed by pump 6 with a flow rate of 25 kg/h to the heat exchanger 4 where it was mixed with steam to reach an outlet temperature of 160°C. The residence time in the heat exchanger 4 was 1.0 sec. The matrix was pumped by pump 7 with a flow rate of 34.5 kg/h to Kettle 3 where the solved β-carotene was mixed with the matrix and emulsified in it. The emulsion was cooled down to 60°C in heat exchanger 5.

[0047] Isopropyl acetate was removed from the emulsion by using a vertical evaporator. The resulting emulsion showed a particle size of the inner phase of 220 nm and was spray dried.

[0048] The final product had a β-carotene content of 11.3%; E1/1: 1159, λ max. 440-460 nm. The powder was well soluble in water. The solution had a very intensive yellow color.

Example 4

Solvent: isopropyl acetate, direct heat transfer (steam).

[0049] 9.25 kg of Fish gelatin, 18.5 kg of sugar and 2.5 kg of ascorbyl palmitate were dissolved in 30.25 kg of water in Kettle 1. The pH-value of this matrix was adjusted with NaOH (20%) to 7.2 -7.6.

[0050] 6.0 kg of β-Carotene, 0.75 kg of dl-α-tocopherol and 3.0 kg of corn oil were dispersed in 30.0 kg of isopropyl acetate in Kettle 2.

[0051] The β-carotene suspension was fed by pump 6 with a flow rate of 20 kg/h to the heat exchanger 4 where it was mixed with steam to reach an outlet temperature of 158°C. The residence time in the heat exchanger 4 was 1.3 sec. The matrix was pumped by pump 7 with a flow rate of 30.4 kg/h to Kettle 3 where the solved β-carotene was mixed with the matrix and emulsified in it. The emulsion is cooled down to 60°C in heat exchanger 5.

[0052] Isopropyl acetate was removed from the emulsion by using a vertical evaporator. The resulting emulsion showed a particle size of the inner phase of 240 nm and was spray dried.

[0053] The final product has a β-carotene content of 11.2%, E1/1:795, λ max. 440-460 nm. The powder was well soluble in water, the solution has a very intensive red color.

Example 5

Solvent: methylene chloride, direct heat transfer (steam).

[0054] 9.25 kg Fish Gelatin, 18.5 kg of sugar and 2.5 kg of Ascorbyl palmitate were dissolved in 30.25 kg of water in Kettle 1. The pH-value of this matrix was adjusted with NaOH (20%) to 7.2 - 7.6.

[0055] 6.0 kg of β-Carotene, 0.75 of kg dl-α-tocopherol and 3.0 kg of corn oil were dispersed in 30.0 kg of methylene chloride in Kettle 2.

[0056] The β-carotene suspension was fed by pump 6 with a flow rate of 20 kg/h to the heat exchanger 4 where it was mixed with steam to reach an outlet temperature of 145°C. The residence time in the heat exchanger 4 was 1.3 sec. The matrix was pumped by pump 7 with a flow rate of 30.4 kg/h to the Kettle 3 where the solved β-carotene was mixed with the matrix and emulsified in it. The emulsion was cooled down to 35°C in heat exchanger 5.

[0057] Methylene chloride was removed from the emulsion by using a vertical evaporator. The resulting emulsion showed a particle size of the inner phase of 196 nm and was spray dried.

[0058] The final product has a β-carotene content of 9.9%, E1/1: 1120, λ_{max}: 440-460 nm. The powder was well soluble in water, the solution has a very intensive yellow color.

Claims

1. A continous process for the preparation of a pulverous carotenoid, retinoid or natural colourant preparation, wherein the active ingredient is finely divided, which process comprises the steps of

a) forming a suspension of the active ingredient in a water-inmiscible organic solvent optionally containing an antioxidant and/or an oil,
b) feeding the suspension of step a) to a heat exchanger and heating said suspension to 100-250°C, whereby the residence time in the heat exchanger is less than 5 sec,
c) rapidly mixing the solution of step b) at a temperature in the range of 20-100°C with an aqueous solution of a swellable colloid optionally containing a stabilizer,
d) removing the organic solvent and
e) converting the dispersion of step d) into a pulverous preparation.

2. A process according to claim 1, wherein the active ingredient has a particle size of less than 1.0 micron, preferably less than 0.4 micron.

3. A process according to claim 1 or 2, wherein the temperature of step b) is 120-180°C, preferably 140-170°C and the temperature of step c) is 50-80°C.

4. A process according to any one of claims 1-3, wherein the residence time in the heat exchanger is 0.5-4 sec, preferably 1-3 sec..

5. A process according to any one of claims 1-4, wherein the water-inmiscible organic solvent is dimethyl carbonate, ethyl formate, ethyl-, or isopropylacetate, methyl-tert. butylether or methylene chloride.

6. A process according to any one of claims 1-5, wherein the active ingredient is a carotenoid.

7. A process according to claim 6, wherein the carotenoid is selected from the group consisting of beta-carotene, beta-apo-4'-carotenal, beta-apo-8'-carotenal, beta-apo-12'-carotenal, beta-apo-8'-carotenic acid, astaxanthin, canthaxanthin, zeaxanthin cryptoxanthin, citranaxanthin, lutein, lycopene, torularodin-aldehyde, torularodin-ethylester, neurosporaxanthin-ethylester, zeta-carotene or dehydroplectaniaxanthin.

8. A process according to any one of claims 1-7, wherein the swellable colloid is selected from the group consisting of gelatin, starch or starch derivatives, dextrin, pectin, gum arabic, octenylbutanedioate amylodextrin, milk protein, vegetable protein as well as mixtures thereof.

9. A process according to any one of claims 1-8, wherein the antioxidant is selected from the group consisting of ascorbic acid, ascorbylpalmitate, dl-alpha tocopherol, mixed tocopherols, lecithine, butylhydroxytoluol, butyl-4-methoxy-phenol and combinations of these compounds.

10. A process according to any one of claims 1-9, wherein the solution of the active ingredient is effected either indirectly through the heat exchanger or directly by mixing with steam and the precipitation of the active ingredient in the swellable colloid is effected continuously in a mixing device connected in series.

11. A pulverous preparation prepared by a process as claimed according to any one of claims 1-10 and containing from 0.5-25% by weight of an active ingredient.

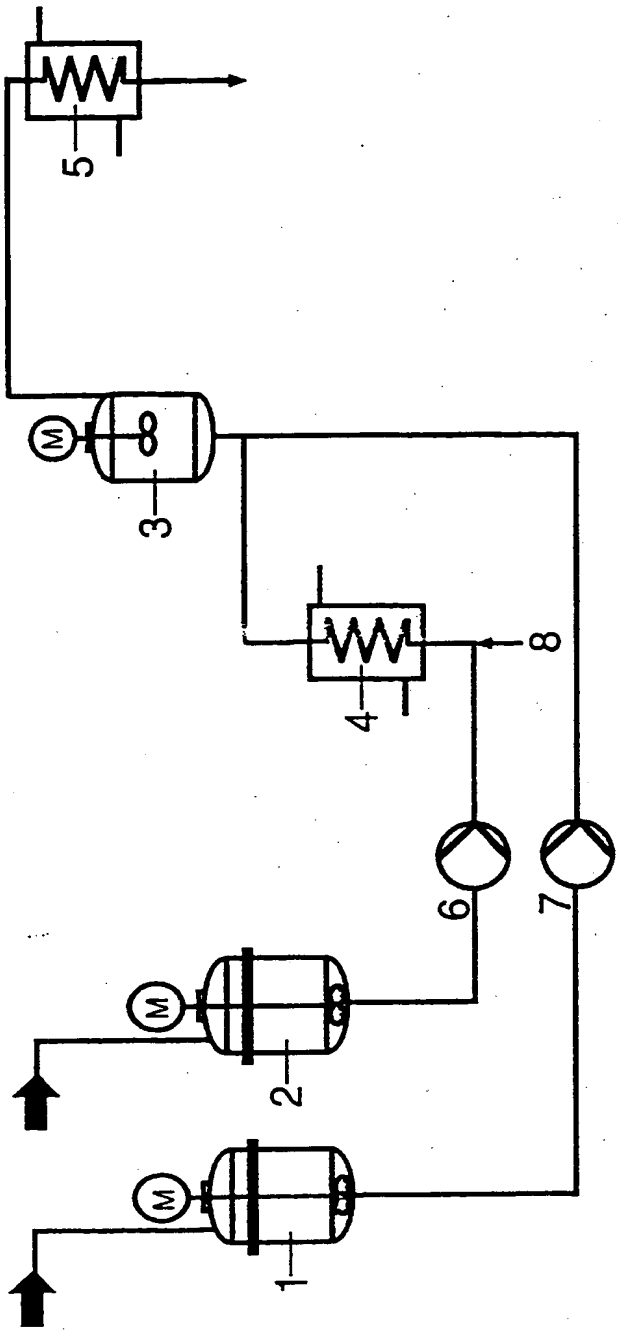

Fig. I

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 10 3239

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 3 790 688 A (WALTER W ET AL) 5 February 1974 * claim 1 *	1-11	A23L1/275
X	US 4 844 934 A (LUEDDECKE ERIK ET AL) 4 July 1989 * examples 1,2 *	1-11	
X	US 5 364 563 A (CATHREIN ERNST ET AL) 15 November 1994 * column 3, line 33 - line 36; examples 1,2 *	1-11	
X,D	US 4 726 955 A (HORN DIETER ET AL) 23 February 1988	1-11	
Y	* examples 1-8 *	1-11	
X	US 4 522 743 A (HORN DIETER ET AL) 11 June 1985 * examples 1-17 *	1-11	
X,D	US 3 998 753 A (ANTOSHKIW THOMAS WILLIAM ET AL) 21 December 1976 * examples 1-4 *	1-11	TECHNICAL FIELDS SEARCHED (Int.Cl.6) A23L
X	DE 12 11 911 B (HOFFMANN-LA ROCHE & CO AG) 3 March 1966	1-11	
Y	* column 3, line 41 - line 53; examples 1-6 *	1-11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	6 May 1999	Bendl, E

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 99 10 3239

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

06-05-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3790688 A	05-02-1974	NONE	
US 4844934 A	04-07-1989	DE 3610191 A	01-10-1987
		AU 593081 B	01-02-1990
		AU 7062887 A	01-10-1987
		DE 3779466 A	09-07-1992
		EP 0239086 A	30-09-1987
		JP 7096649 B	18-10-1995
		JP 62240364 A	21-10-1987
US 5364563 A	15-11-1994	AT 96312 T	15-11-1993
		DE 59003205 D	02-12-1993
		DK 410236 T	13-12-1993
		EP 0410236 A	30-01-1991
		JP 2572877 B	16-01-1997
		JP 3066615 A	22-03-1991
US 4726955 A	23-02-1988	DE 3611229 A	08-10-1987
		DE 3784534 A	15-04-1993
		DK 170287 A	05-10-1987
		EP 0239949 A	07-10-1987
US 4522743 A	11-06-1985	DE 3119383 A	02-12-1982
		AT 16814 T	15-12-1985
		AU 553623 B	24-07-1986
		AU 8372582 A	18-11-1982
		CA 1202809 A	08-04-1986
		DK 216082 A,B,	16-11-1982
		DK 334188 A,B,	17-06-1988
		EP 0065193 A	24-11-1982
		JP 1670100 C	12-06-1992
		JP 3035347 B	27-05-1991
		JP 57195161 A	30-11-1982
US 3998753 A	21-12-1976	AT 351912 B	27-08-1979
		AT 625675 A	15-01-1979
		BE 832331 A	12-02-1976
		DE 2534091 A	26-02-1976
		FR 2281961 A	12-03-1976
		GB 1502895 A	08-03-1978
		JP 51041732 A	08-04-1976
		NL 7509586 A	17-02-1976
DE 1211911 B		NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82